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Cyclic Oxidation Behavior of Plasma Nitrided Valve Steel

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Abstract

The cyclic oxidation behavior of DIN 1.4871 austenitic valve steel was investigated after plasma nitriding. For this, nitriding cycle of 450°C for 7h was carried out. Cyclic oxidation of nitriding samples and base metal were evaluated at 750°C. The results of this investigation indicated that plasma nitriding strongly affected the oxidation resistance of the samples. The nitrided layer which is comprised predominantly a "S" phase, offered superior oxidation resistance. The mechanism of oxidation is explained by outward diffusion of metallic cations (Cr and Fe) and reaction with oxygen on the surface of specimens. This mechanism is confirmed by EDX analyses.

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Key words: *Plasma Nitriding, Valve Steel, Oxidation Resistance*

1. Introduction

Valves are among the most important components of engines. They regulate both the intake of air for the combustion process and the discharge of the exhaust gases generated in the combustion chamber. Usually intake valves and exhaust valves are made of martensitic and austenitic steels, respectively [1, 2]. The materials and processes used for valves must be particularly with respect to two criteria; high temperature stability and wear resistance [3]. In recent years, there has been an increased interest in nitriding process for improving the performance of valve steel [4, 5]. However, salt bath nitriding and conventional gas nitriding could not be effectively performed on austenitic steels due to presence of a tenacious oxide on the surface [6].

On the other hand, plasma nitriding is among the surface engineering techniques which have been successfully applied to these alloys [7, 8]. During the first stage of plasma nitriding process, the sputtering action of energetic atoms and ions effectively removes the surface oxide film (Cr_2O_3), thus accelerates the nitrogen mass transfer. Accordingly, plasma nitriding can be carried out at lower temperatures and higher rates than conventional nitriding processes [9].

Plasma nitriding carried out at normal temperatures of 500°C and above, causes precipitation of chromium nitrides and subsequently leads to depletion of chromium content of the austenite matrix and significantly reduces the corrosion resistance [6, 10]. Therefore, to avoid deterioration of the substrate properties, lower temperature plasma nitriding has been suggested to be responsible for producing a high hardness thin layer on stainless steels together with good corrosion resistance [11-13].

The austenitic steels in automotive exhaust valves are subjected to temperatures up to 750°C [1, 2] and cyclic high temperature oxidation resistance is considered as an essential requirement. Nevertheless, there

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is almost no published work to report the influence of nitriding on oxidation behavior of valve steels. Moreover, the application of low-temperature plasma nitriding for highly alloyed austenitic steels has not been sufficiently clarified.
The aim of the present study is to examine the cyclic high temperature oxidation behavior of plasma nitrided valve steels and to optimize the process parameters for nitriding 1.4871 austenitic steel which is widely used in automotive industry.

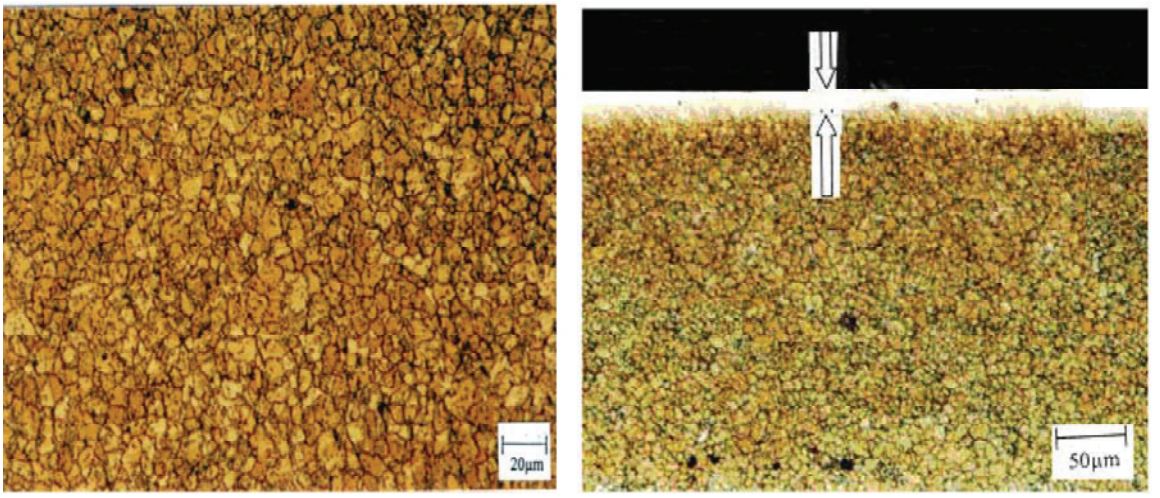
2. Experimental procedure

The material used for this investigation was Din 1.4871 valve steel with the composition of 0.47-0.53% C, 9% Mn, 20-22% Cr, 3.5-4.3% Ni, <0.1% Si and balanced by Fe. Pin type specimens of 5 mm diameter and 20 mm in high were prepared for wear testing. For cyclic oxidation tests, cylindrical specimens were prepared with 10mm diameter and 10mm thickness. Before nitriding, the samples were ground and polished with standard metallographic techniques.
The specimens were nitrided in a 5kw DC discharge plasma nitriding unit for 7h at 450°C, by using a gas composition of 25 vol% nitrogen and 75 vol% hydrogen at a pressure of 4 mbar. Sputtering treatment was carried out with argon and hydrogen with ratio1:1 for 30 minute before nitriding.
High temperature oxidation tests were carried out at 750°C using 30 minute cycles and in air furnace at atmospheric pressure. After each cycle, samples were cooled in air and the weight change was accurately determined.
The microstructure of the cross sections of the treated samples was studied by optical metallographic techniques and scanning electron microscopy (SEM). X-ray diffraction analysis was employed to identify the phases present in the surface layers. Surface hardness of the treated samples was measured by Vickers micro-hardness tester at a load of 25 gf. The values quoted are the average of at least 5 readings. After cyclic oxidation testing, scanning electron microscopy (SEM) equipped with EDS facilities were used to examine the worn and oxidized surfaces and subsurface.

3. Results and discussion

3. 1. Composition and structure of layers

Typical optical micrographs of the BM and nitrided layer produced at 450°C are shown in Figure. 1. Table 1 summarizes the phase compositions, thickness, surface roughness and hardness of the nitrided layer. The structure of the austenitic steel before nitriding contains equiaxed grains with uniform carbide precipitates. It can be seen from Figure. 1b that nitriding at 450°C produces a white layer that is unaffected by the marble etchant. X-ray diffraction pattern of nitrided sample is shown in the Figures 2. By attention to Figure 2, it is resulted that the layer produced at 450°C contains a different phase from that of the higher temperature layers. This phase, named as expanded austenite (γ_N), or “S” phase, is a supersaturated (20-30 at %) solid solution of nitrogen in austenite with a distorted FCC structure. A large number of research papers have been published on production and properties of this phase in austenitic stainless steels [11-13]. The “S” phase is thermodynamically metastable and has a larger lattice parameter than the substrate austenite [28, 29].



(a). Untreated valve steel (b). 450 ^0C

Figure. 1. Optical micrographs of (a) Untreated valve steel and (b) Nitrided sample at 450°C for 7 hours.

Table 1. Summary properties of plasma nitrided sample.

Properties	7 hours, 450°C
Microtructure	"S" phase
Thickness(μm)	20
Hardness, (HV_{25gf})	1100
Roughness, R_a (μm)	0.15

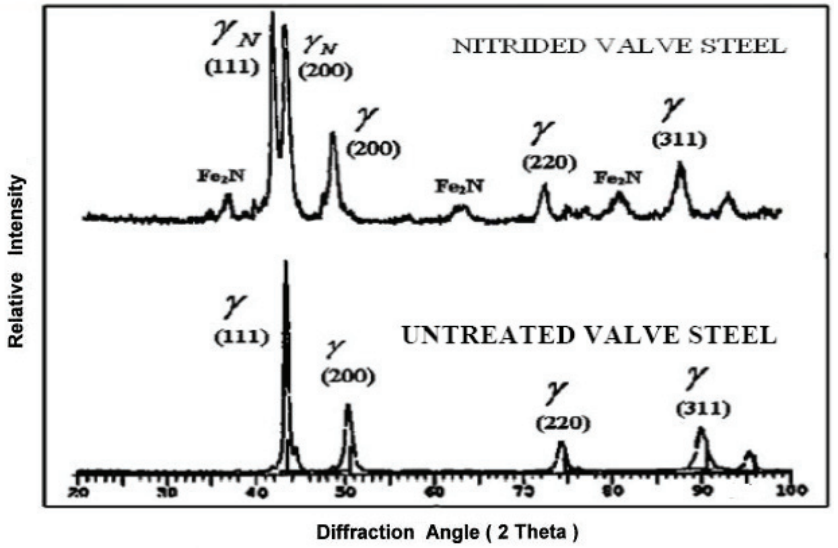


Figure 2. X-ray diffraction patterns of the valve austenite steel sample and nitrided sample at 450°C for 7 hours.

3.2. Oxidation behavior

Figure 3 shows the weight gain versus the number of cycles of untreated and nitrided specimens during cyclic oxidation tests at 750°C in air. The curves indicate that nitriding at 450°C (low temperature nitriding) has lower weight gain compared to untreated specimens. For the nitrided specimen at 450°C, a parabolic law rate was observed from the beginning to the end of cyclic testing with the lowest amount of oxidation. Thus, it appears that plasma nitriding at 450°C has a beneficial effect on the oxidation rate of the valve steel. This is confirmed according to Figure 4.

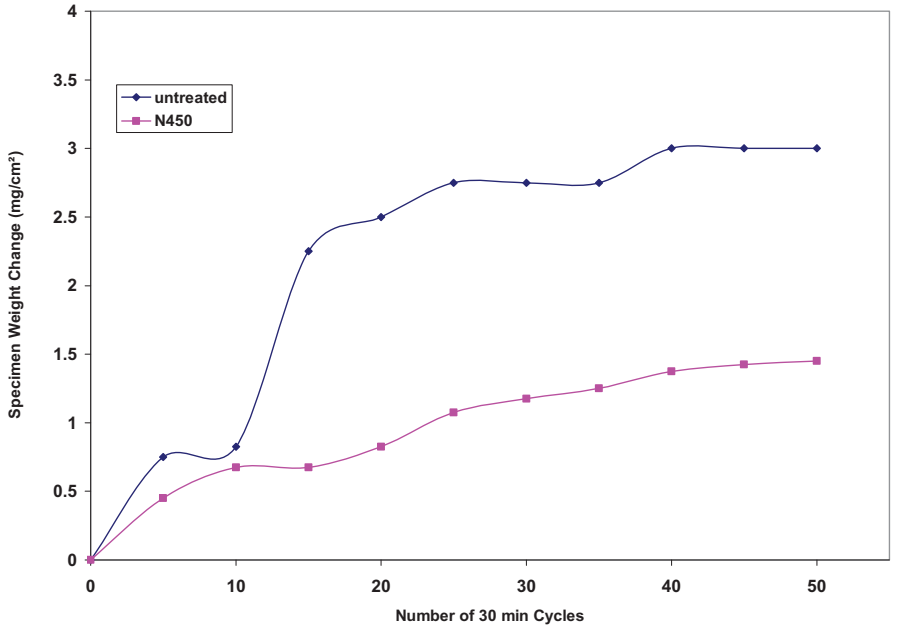


Figure 3. Weight change for untreated and nitrided specimens in 30min cycles at 750°C.

Figure 4. High cyclic oxidation resistance of 450°C plasma nitrided specimen in 30min cycles at 750°C.

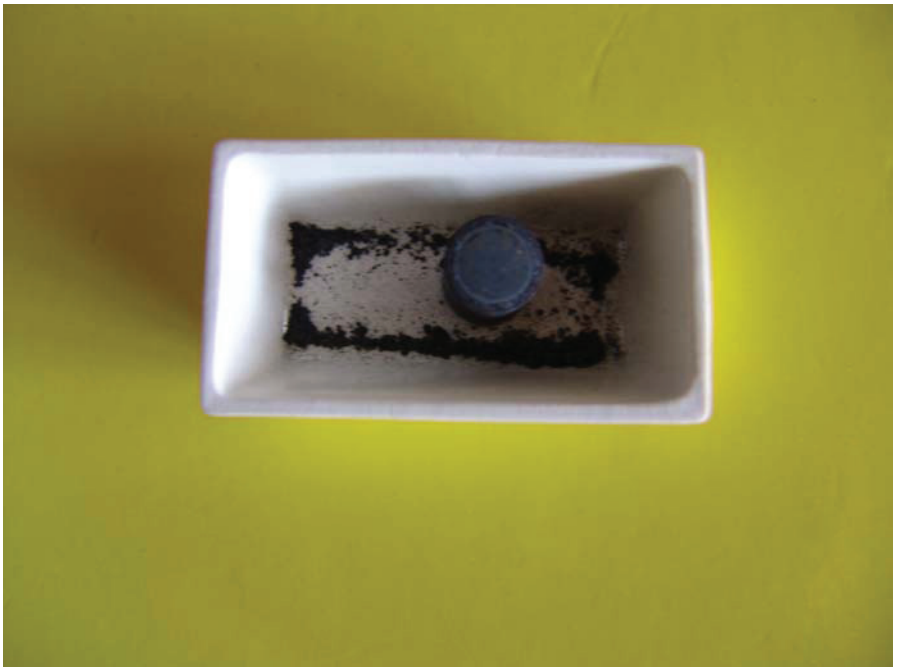
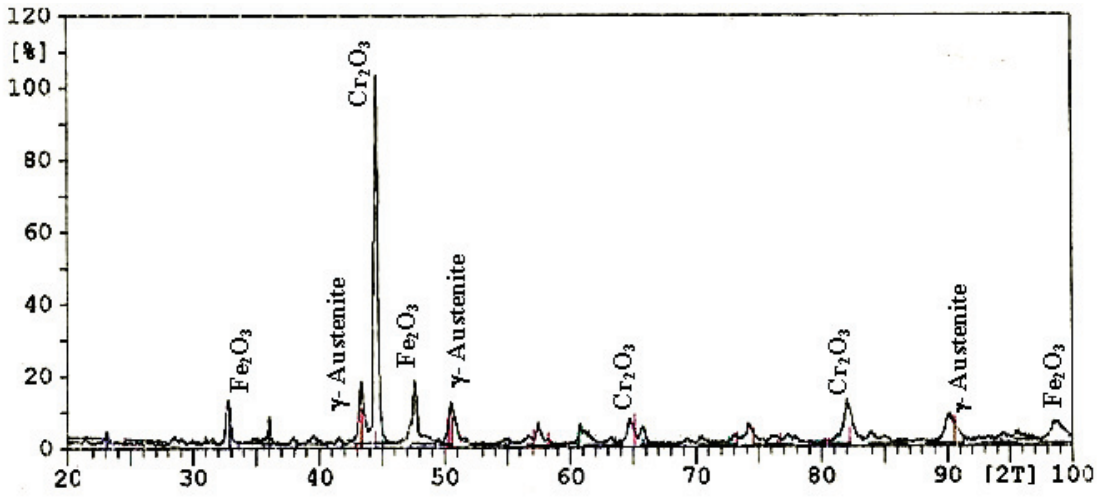
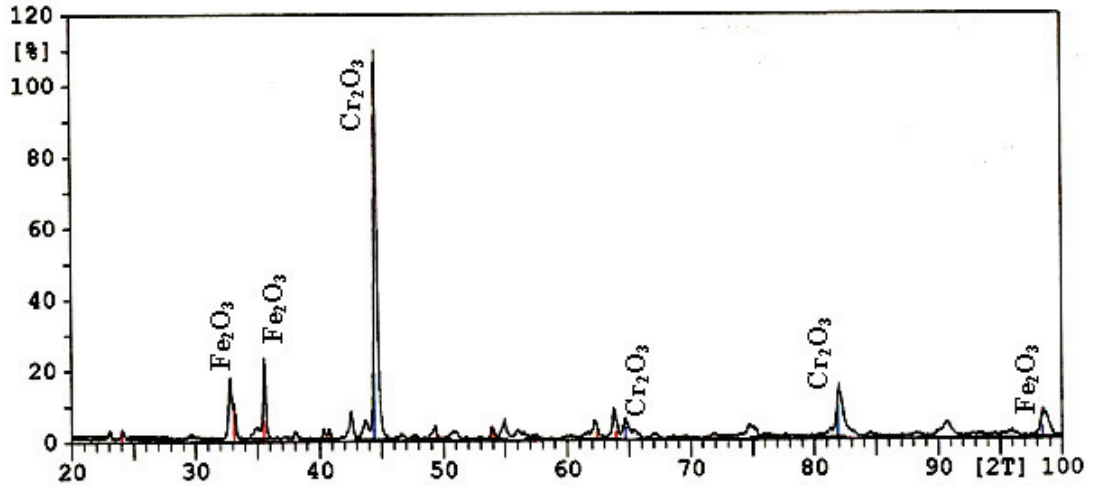


Figure 5 shows the XRD spectra of the untreated and nitrided specimens after being oxidized for 50 cycles. The X-ray patterns prove that the oxide scale formed on both the untreated and the 450°C plasma nitrided samples is mainly Cr_2O_3, together with a spinel of chromium and iron ($FeCr_2O_4$). It is generally accepted that one of the best oxides for protecting the alloy against corrosion up to temperatures of around 1000K is Cr_2O_3 since diffusion through it is much slower compared to other oxides such as Fe_2O_3 [14]. Pleshivtsev [15] explained that the grain boundary diffusion could be favored by ion implantation. In the case of the plasma nitriding at 450°C, nitridation induces some deformation within the crystal structure, leading to a surface region with fast-diffusion paths which favor the chromium transport and the formation of a dense protective chromium-rich scale. This phenomenon has been proposed and reported by other researchers [16]. Formation of a dense, adherent chromium oxide scale can explain the higher oxidation resistance of 450°C plasma nitrided specimen at 750°C (Figure 6).



(a)



(b)

Figure. 5. X-ray pattern of unnitrided and plasma nitrided specimens after cyclic oxidation at 750°C.

Figure 6 shows SEM micrographs of surface morphology of the oxide scales developed on the untreated and nitrided specimens after cyclic oxidation testing at 750°C together with the results of EDS microanalyses. For unnitrided and 450°C nitrided specimens, a compact oxide layer is observed on the surface. EDS analyses show the enrichment of chromium on these oxidized surfaces. The mechanism of oxidation could be explained by outward diffusion grain boundaries of metallic cations (Cr and Fe) and reaction with oxygen on the surface of specimen (Figure. 7). As a consequence of this diffusion mechanism, a parabolic rate law is expected [14, 15].

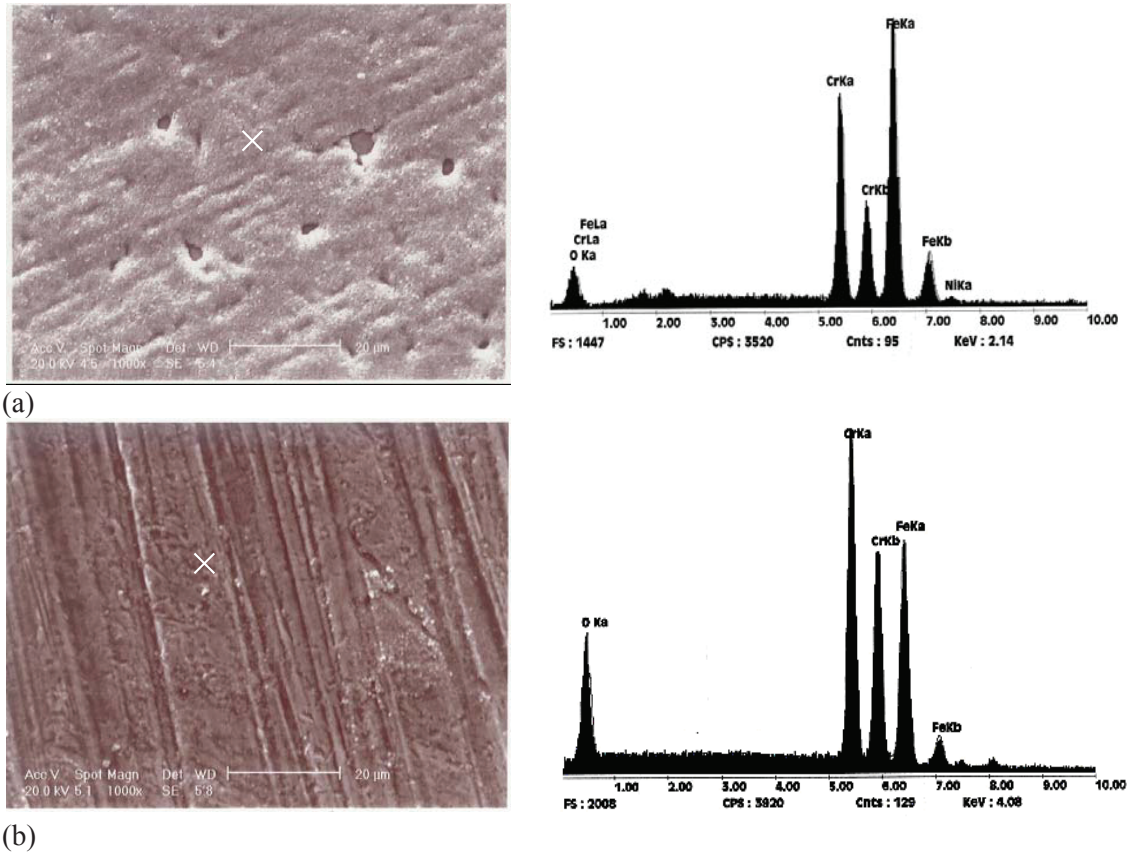


Figure 6. SEM micrographs and EDS spectra of the surface on specimens oxidized at 750°C, in air.
(a) Un-nitrided specimen
(b) 450 nitrided specimen

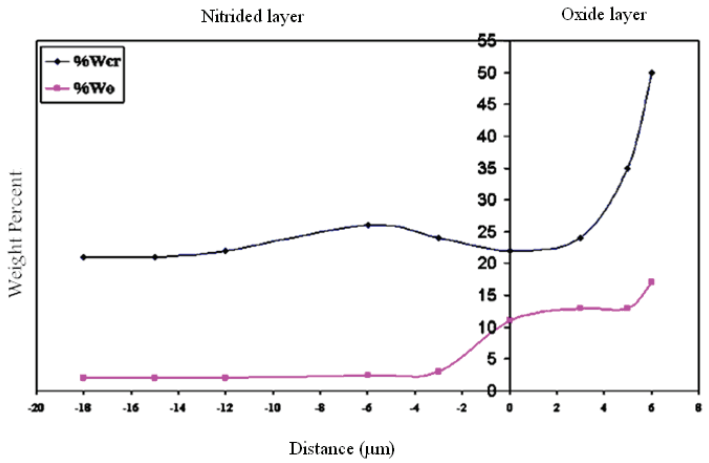


Figure. 7. Chromium concentration changes for nitrided specimen in different zone after of oxidization.

4. Conclusions

1. Plasma nitriding at 450°C produced a modified layer on the austenitic valve steel which was identified as a metastable phase known as S-phase.
2. Cyclic oxidation resistance of the austenitic valve steel increased after plasma nitriding at 450°C. This was attributed mainly to the formation of a compact oxide layer enriched of chromium on its oxidized surface.
3. The mechanism of oxidation could be explained by outward diffusion grain boundaries of metallic cations (Cr and Fe) and reaction with oxygen on the surface of specimen.

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